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AFML-TR-77-91

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POLYMER CHARACTERIZATION USING TG-MS TECHNIQUES

RESEARCH APPLICATIONS DIVISION
SYSTEMS RESEARCH LABORATORIES, INC.
2800 INDIAN RIPPLE ROAD
DAYTON, OHIO 45440

APRIL 1977

TECHNICAL REPORT AFML-TR-77-91
Final Technical Report for Period April 1976 — March 1977

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This technical report has been reviewed and is approved for publication.

I. J. GOLDFARB
Project Monitor

FOR THE COMMANDER

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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A series of polymers has been analyzed using TG-MS techniques. Detection and identification of volatile gases evolved under programmed heating rates are correlated with sample weight loss to provide information concerning polymer stability. For the case of a series of perfluoro- and perfluoroether-substituted bibenzoxazole elastomers, a mechanism of thermal degradation is proposed.

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PREFACE

This report was prepared by Dr. E. Grant Jones, Mr. Paul A. Benadum, and Mr. Donald L. Pedrick of the Research Applications Division of Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, Ohio 45440, under Contract F33615-76-C-5152. It was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Ivan J. Goldfarb (AFML/MBP) as Project Scientist.

The studies outlined in this report were conducted in the Air Force Materials Laboratory during the period April 1976 - March 1977.

The authors would like to acknowledge the efforts of Mrs. Marian M. Whitaker of the Research Applications Division who made editorial comments on the reports. Valuable discussions with several of the scientists in the Polymer Branch of the Air Force Materials Laboratory--in particular, Dr. Ivan J. Goldfarb and Dr. Robert C. Evers--were instrumental in the analysis of samples.

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SECTION I

INTRODUCTION

The behavior of polymers at elevated temperatures is an important criterion for determining their utility in aircraft or missile systems. Important polymeric properties must not change drastically over the wide temperature ranges that may be encountered in operation. It is extremely difficult to predict under which conditions a polymer will cease to function at the desired level of efficiency. If the extreme conditions are those of temperature, one of the most powerful techniques for determining physical-chemical changes that will be deleterious to the required functions involves the use of thermogravimetric mass spectrometry (TG-MS); with this technique sample loss under controlled heating conditions is correlated with analysis of volatile species evolved.

Knowledge of decomposition products is the first step in the determination of a degradation mechanism. By analyzing the products and the conditions under which degradation occurs, important insight into the chemical changes can be gained. Some understanding of the chemistry of the degradation process makes possible the prediction of new designs for more stable systems. In this manner general stability criteria are evolved which may serve in the design and production of polymers for use over an extended operational temperature range. Extension of the temperature stability range is economical and provides a wider margin for fail-safe operation in a critical environment.

The combined TG-MS technique is very sensitive in the detection of solvents or other impurities trapped in the polymeric matrix. Hence, this technique is invaluable for quality control as well as for tracing the chemical changes taking place at elevated temperatures.

This report covers the results of analyses performed during the period April 1976 - March 1977 and provides a final reporting of data obtained under Contract F33615-76-C-5152.

SECTION II

INSTRUMENT STATUS

A few minor modifications to the instrument (see schematic in Fig. 1) were introduced to improve overall performance; these are outlined below:

1. Water-cooling lines were replaced with copper tubing.
2. Faulty water pump and diffusion pump heater were replaced.
3. Dry nitrogen was used in the venting procedure to effect faster pumpdown time.
4. Some of the components involved in electronic modifications outlined in a previous report (AFML-TR-76-210) have been assembled and tested.
5. A design for an improved quadrupole housing has been prepared. This new design will permit more efficient pumping of the quadrupole system and will result in increased overall system sensitivity.

SECTION III

EXPERIMENTAL RESULTS

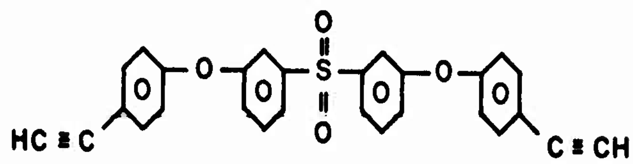
Over the period covered by this report, 22 different polymers have been analyzed. Table 1 gives the sample identification number and references the appropriate analysis report. This is followed by abbreviated versions of the analysis reports submitted previously. All figures displaying weight loss, total-ionization, or specification behavior as a function of temperature have been deleted.

A manuscript has been prepared on the analysis of the thermal degradation of a series of perfluoro- and perfluoroether-substituted bibenzoxazoles. This manuscript is included as an appendix.

TABLE 1. SUMMARY OF POLYMER SAMPLES ANALYZED

Sample Number	Analysis	
	Experiment Number	Report Number
RPS	102, 104	III H - 76
PSF	103	III I - 76
R/PS/F-25FD	106	III J - 76
T56384-24	105	III K - 76
R/PS/F-DMAC	108	III L - 76
HR-600/AS	107	III M - 76
Browning 3S01/AS	109	III N - 76
S208/T300	110	III O - 76
30R/PS/F	114	III P - 76
S-100	115	III Q - 76
Plex II	116	III R - 76
Stretched Acrylic	117	III S - 76
PP6-112	113	III T - 76
37-3AS	127	III U - 76
Clad-4	128	III V - 76
GAC590	129	III W - 76
SL2000	126	III X - 76
BR-4-28	130	III Y - 76
4PAS-A	131	III Z - 76
BATQ-H	132	III AA - 76
4PAS-C	133	III BB - 76
FM-73	134	IV A - 77

RPS



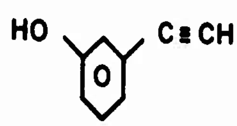
1. Using data from MTA 104,

Sample Weight	3.77 mg
Weight Lost	2.62 mg
Residue	1.15 mg

Of the total weight lost, 54% corresponds to a low-temperature process and 46% to higher-temperature process. These are clearly shown in the weight loss and its first derivative.

2. The low-temperature process maximizes at 180°C with FWHM ~ 40 centigrade degrees. The higher temperature weight loss maximizes at 515°C and covers a much wider temperature range owing to the overlap of several competing and consecutive decomposition processes. Total ionization shows no indication of the former weight loss. It maximizes in the vicinity of the latter (~ 475°C).

3. This is one of the most unique combinations of weight loss and total-ionization behavior observed in this laboratory. There is only fragmentary ionic evidence to identify the species lost at 180°C. Certainly this indicates the loss of non-volatile species. Experimentally, a grey sublimate was observed on the upper (cooler) regions of the quartz hang-down tube. Other available information (DSC) indicates reaction in this temperature region in which the IR bands of the terminal acetylene disappear. The principal ions observed are m/e 118 and 90 probably corresponding to



followed by loss of CO. Since this is a molecular species, it is probably a fragment ion from a larger non-volatile molecule. m-hydroxyphenyl acetylene would be extremely volatile so that if it were released from the hot zone, a complete and intense mass spectrum would be expected. Its absence suggests that the original sample (non-volatile) is sublimating to colder regions of the equipment, resulting in an extremely low probability for ionic detection.

The independent evidence of a chemical reaction may account for the small FWHM for this process by considering a competitive process that results in a product of less volatility that can remain in the hot zone until degradation temperatures are achieved.

4. The higher-temperature weight loss corresponds to a series of volatile products summarized in the following:

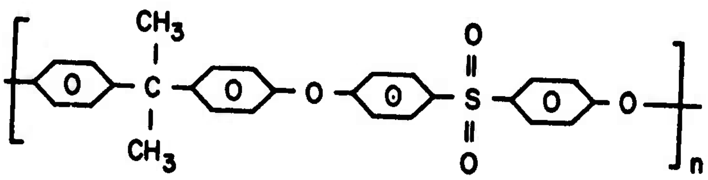
		Temperature (°C)	
Sulfur dioxide	SO_2	490	major
Phenol	ϕOH	485	major
Phenyl ether	ϕOϕ	530	< 10%
Benzene	ϕH	565	< 10%
Alkyl benzenes		565	< 10%
Water, carbon monoxide, methane		600	

These products are all consistent with the expected structure of RPS.

5. There is evidence for CO and H_2 eliminated at higher temperatures (720°C).

Report III I - 76

PSF



1. Sample Weight 4.21 mg
   Weight Lost 3.55 mg
   Char .76 mg

Both total ionization and derivative curves maximize at ~ 500°C.

2. Most of the spectrum is similar to RPS, for example,

		Temperature (°C)
Sulfur dioxide	SO_2	495
Phenol	ϕOH	495
Phenyl ether	$\phi O \phi$	535
Benzene	ϕH	560
Water, carbon monoxide, H_2O, CO		600

This is not surprising since a large portion of the polymer has the same structure as the RPS. It is interesting that the temperatures correspond very closely. This suggests that the RPS polymerizes before the thermal-degradation temperature region is achieved. In addition, there appears to be traces of p-benzyl phenol (as observed from RPS).

3. The major difference between PSF and RPS is that the former releases allene and methane at ~ 500°C.

Report III J - 76

R/PS/F-25FD

Mixture of RPS and PSF

1. The sample displayed major weight loss and degradation maximizing at 190°C. Overall, the products of the degradation are similar to PSF (Report III I).

2. At ~ 80°C, several volatile products were observed. Primarily 1,4 dioxane was released. In addition, there were several other species evolved at the same temperature. Only estimates can be made to identify these. The following are considered as possibilities:

(i) Phenyl acetylene, c.f., m/e 102, 103, 76
(ii) Dimethyl sulfoxide, c.f., m/3 15, 45
(iii) C_9H_8O (?), c.f., m/e 132, 117, 43

3. Identification of 1,4 dioxane and dimethyl sulfoxide is not surprising considering their possible use in sample preparation. The tentative identification of phenyl acetylene may be much more significant of the cross-linking reaction.

Report III K - 76

T56384-24

(Structure not available)

1. The entire sample decomposed thermally below 520°C, leaving no char.

2. Two regions (280°C, 430°C) of definite weight loss are observed. The former involves ~ 14% of the sample and the latter, 86%.

3. The total ionization current maximizes at 430°C, with an unresolved shoulder at lower temperatures. At higher temperatures there is evidence of significant tailing resulting from displacement of some of the previous samples introduced in large quantities.

4. Approximately 50% of the ionic products are CO_2^+, as evidenced by m/e 44 and 22 (CO_2^{++}). This is observed at 280°C and 420°C. There are other ions observed at these temperatures; however, their low intensity relative to CO_2^+ suggests that carbon dioxide is one of the major products. This may arise from thermal decomposition of a carbonate or carbamate. Elimination of CO_2 occurs over a very narrow temperature interval (FWHM ~ 40°C).

5. Commencing at 280°C, water is evolved (~ 10%). Its rate of formation maximizes over the interval 360-400°C and is complete at 470°C.

6. Between 420 and 440°C, there is evidence for phenol production.

7. There is a wide range of silicon-containing ions maximizing over a broad temperature range 430°C to 470°C. The highest mass ion is $(CH_3)_7\ Si_4O_4^+$ (m/e 281). There is a long series of ions representing fragments from methyl siloxanes. Some of the more important ions are $(CH_3)_8Si_4O_7^+$ (m/e 407), $(CH_3)_5\ Si_2O^+$ (m/e 147), $(CH_3)_3\ Si^+$ (m/e 73), and CH_5Si^+ (m/e 45). All of these are characteristic of methyl siloxanes.

8. In summary, carbon dioxide, methyl siloxanes, and water are the major volatile species detected.

Report III L - 76

R/PS/F-DMAC

Mixture of RPS and PSF

1. Total-ionization behavior indicates onset of degradation in the vicinity of 440°C. In the region of interest below degradation temperatures, there is a maximum in volatile sample evolution at 75°C.

2. The weight loss over the temperature interval (44 - 110°C) of the peak is ~ 0.10 mg from a total sample weight of 7.82 mg. The mass spectrum in this temperature region indicates only N, N dimethyl acetamide $CH_3CON(CH_3)_2$.

3. No other evolved species could be detected.

4. The estimated weight fraction of solvent is ~ 1 - 2%.

Report III M - 76

HR-600/AS

(Structure not available)

1. Volatile products were analyzed for sample temperatures up to 480°C. Previous analysis of a sample in this series showed onset of degradation above 480°C.

2. Sample Weight 230.7 mg
Weight Loss 6.5 mg
The total weight loss is ~ 3% of sample.

3. At the highest temperatures, thermal-degradation products such as carbon dioxide are evolved.

4. In the temperature region of interest (pre-degradation), only two products were detected. The solvent N-methyl-pyrrolidone evolved with maximum rate at 370°C. Water was released with a rate maximizing at 420°C.

5. The temperature profiles indicate that the evolution of water and N-methyl-Pyrrolidone is complete prior to the onset of polymer degradation. These products represent about 2% by weight of the original sample.

Report III N - 76

Browning 3S01/AS

(Structure not available)

1. Volatile products evolving from room temperature to 200°C were monitored. The weight loss over this interval is ~ 1% of the total sample weight.

2. There is predominantly one temperature profile maximizing at ~ 60°C that describes the temperature dependence of the majority

of solvents released. In this temperature region, methyl ethyl ketone is the major product; however, there is evidence for another species, possibly methyl acetate, accounting for a large m/e 15.

3. At slightly higher temperatures, there is evidence for traces of ethylamine.

4. Water evolution commences at 100°C and at 200°C its production is still increasing.

Report III O - 76

S208/T300

(Structure not available)

1. Sample weight is 270 mg; weight loss up to 230°C is 5 mg, ~ 2% of sample.

2. There is a broad temperature profile of a mixture of gases released in the vicinity of 115°C. There is very little apparent weight loss over this interval. One possible component in this mixture is isopropyl propionate. All of the observed ions m/e 27, 29, 31, 43, and 57 are common to a wide range of C, H, and O-containing species.

3. Acrolein CH_3CHCHO evolves at higher temperatures with a rate maximizing in the vicinity of 210°C. This corresponds to the region of rapid weight loss.

4. Over a similar region 160 - 230°C, water evolves. At the highest temperature in this experiment, the rate of water production is still increasing. Acrolein and water comprise ~ 2% by weight of the sample.

Report III P - 76

30R/PS/F

Mixture of RPS and PSF

1. Analysis for volatile products was made over the range from room temperature to 180°C.

2. A weight loss of 0.38 mg representing ~ 4% of the sample was observed.

3. The total ionization curve indicates two maxima at 64 and 150°C. The former arises from the release of solvent in particular dioxane. Additional impurities as evidenced by a large m/e 89 peak (possibly $C_4H_9S^+$) are also present. The latter maximum corresponds to the release of water. The water evolution rate has decreased considerably at 180°C.

4. Identification of the other trace impurities necessitates the use of larger sample weights. The overall sensitivity and signal-to-noise ratio is poor for weight losses less than 0.5 mgm.

Report III Q - 76

S-100

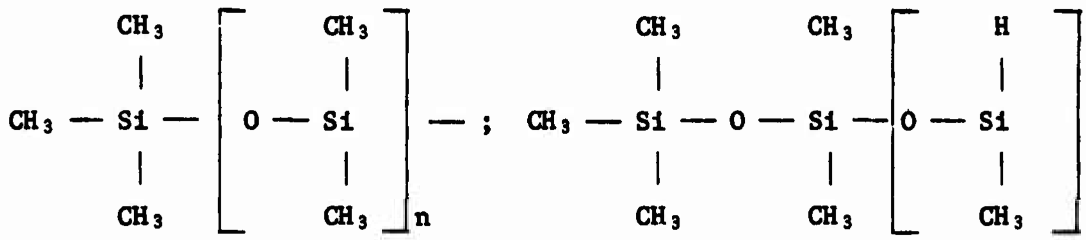
(Structure not available)

1. The sample was analyzed from room temperature to 180°C. Over this temperature interval 2.6 mg of the original sample weight of 675.66 mg was lost as volatile products.

2. Water evolved commencing at ~ 60°C and its rate of production maximized at 84°C then dropped slowly over the rest of the temperature interval.

3. The total ionization behavior indicated a maximum rate of volatile products formation at ~ 107°C.

4. Commencing at ~ 50°C fragment ions from a series of methyl siloxanes were observed. Their intensity maximized at 107°C and remained approximately constant up to 180°C. The major ions can be represented by the structures



n = 0, 1, 2

These ions are characteristic of low molecular weight solaxanes. Ions up to m/e 281 [$(CH_3)_7Si_4O_2^+$] could be assigned to methyl siloxanes.

Report III R - 76

Plex II

(Structure not available)

1. Analysis covered the temperature range from 30-175°C. From the initial sample weight of 670.25 mg about 3.3 mg (0.5%) was lost at 175°C.

2. The onset of ions corresponded to the first detectable weight loss at ~ 54°C. The total ionization current displays a sharp maximum at 144°C. The intensity decreases by a factor of two at 170°C.

3. The only detectable species at 144°C is water comprising ~ 95% of the total ionization measured at that temperature.

4. Degradation products are observed starting at 115°C; their intensity achieves a maximum near the highest temperatures of the present experiment. The predominant species observed is methyl methacrylate; although other products are present in lesser abundance (cf. m/e 121). Identification of these would require the use of GCMS techniques.

Report III S - 76

Stretched Acrylic

(Structure not available)

1. Analysis over the temperature range 30-190°C was made to identify solvents and other pre-degradation products.

2. Sample weight 470.21 mg
   Weight loss 3.5 mg ~ 0.7%

3. The total ionization curve displays an onset at 40°C and a maximum in the vicinity of 160°C.

4. Overall the results of this MTA No. 117 are very similar to those for MTA No. 116; however, in the present analysis the signal/noise ratio is much higher.

5. There are some products evolved at ~ 100°C in very low abundance. The major ions showing this temperature behavior are 51, 57 and 77 characteristic of a wide range of compounds.

6. Water begins to evolve at 40°C and its rate of formation maximizes at 150°C. Because of its high abundance the temperature profile of water approaches very closely that for the total ionization current.

7. Formaldehyde (CH_2O) is released at the higher temperatures showing a pronounced maximum at 166°C.

8. As with the previous sample methyl methacrylate evolves at the highest temperatures. In this case the rate of production does not maximize in the temperature interval of the present study; it continues to increase to 190°C.

Report III T - 76

PP6-112

(Structure not available)

1. Volatile products released in the temperature interval from room temperature to 190°C.

2. Only 0.2% (2.1 mg) of the original sample weight (917.01 mg) was lost during the experiment.

3. The total ionization current maximizes at 97°C.

4. Water is evolved with a rate maximizing in the vicinity of 75°C.

5. The total ionization current peaks near the apparent onset for weight loss.

6. Above 75°C there is a series of volatile products having similar temperature profiles. The low sensitivity and complexity of mass spectral pattern precludes positive identification of the released gases. This problem is ideally suited to GCMS techniques in which products are separated prior to mass spectral analysis. A mass spectrometer is not ideally suited for analysis of mixtures.

Report III U - 76

37-3AS

(Structure not available)

1. At the request of the submitter, the method of sample heating was altered. The sample temperature was raised from 30°C to 200°C in ~ 35 minutes; then the temperature was maintained in the vicinity of 200°C for another hour.

2. Sample Weight 48.8 mg
   Weight Loss 0.14 mg (0.3%)

3. The onset of volatile products occurred at ~ 70°C and these maximized at ~ 176°C. The total ionization current closely matched the weight loss.

4. Water is the predominant species evolved. The temperature profile indicates an onset at 75°C and maximum at 160°C. Water comprises 70% of the volatiles detected.

5. Although other ions such as m/e 20, 28 and 44 were present in high abundance, they could not be definitely assigned to the present sample. The preceding experiments involved a similar format, namely ten times higher sample weight and reduced temperature scan. Ideally, to remove traces of previous samples, the furnace should be raised to 1000°C. When such large amounts of sample are used, it is not desirable to thermally decompose the entire sample. As a result memory effects can interfere with the analysis.

RECOMMENDATIONS

1. Although it can be time consuming, it may be advisable in studies of this type to cycle the furnace to 1000°C after removal of sample to facilitate cleaning the system of products condensed on the walls.

2. Plans are underway to relocate the mass spectrometer closer to the multiple cross to provide a direct line of sight between sample and detector. This will aid in the detection of low vapor pressure products and should provide greater overall sensitivity.

Report III V - 76

Clad-4

(Structure not available)

1. Sample Weight 293.8 mg
   Weight Loss 3.5 mg (1.2%)

2. The predegradation products (solvents and trapped gases) released over the temperature range 20-190°C were analyzed.

3. Products are detected at temperatures as low as 50°C. Water is the principal product maximizing at 130°C. At this temperature water accounts for ~ 65% of the ions detected. There are indications of traces of nitrogen, oxygen and carbon dioxide in this vicinity, with abundance less than 10% that of water.

4. There is evidence for degradation products commencing at 100°C. Their rate of production continues to increase above 190°C.

Report III W - 76

GAC590

(Structure not available)

1. Sample Weight 357.2 mg
   Weight Loss 2.8 mg (0.8%)

2. The total ionization profile indicates the onset of detectable products at 45°C and a linear increase in product abundance up to 200°C. Since sample weight is approximately 100 times the normally used amount the experiment is truncated before the majority of the sample thermally decomposes.

3. Thermal degradation commences at ~ 140°C. Water evolution starts at ~ 50°C and the rate increases rapidly maximizing at ~ 180°C. At the maximum, water ions m/e 16, 17 and 18 comprise 86% of all ions observed. The other major ions present are m/e 28, 44.

4. As with the previous sample (cf. Report III V), oxygen evolves in trace amounts following the temperature profile established by water.

Report III X - 76

SL2000

(Structure not available)

1. Temperature range 30-200°C

   Sample Weight 138.5 g
   Weight Lost .6 g (i.e., 0.4%)

2. From the total ionization behavior, thermal degradation occurs rapidly above 150°C. The total weight loss below 150°C (~ 0.1%) appears to arise solely from the onset tail of thermal degradation.

3. The smooth onset of weight loss gives no indication of the release of pre-degradation products.

Report III Y - 76

BR-4-28

(Structure not available)

1. Sample Weight 5.14 mg

   Weight Loss 3.36 mg (61%)

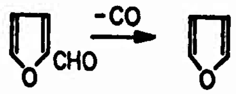
   Temperature Range 30-1000°C

2. The degradation of this sample is quite complex. However, there is excellent correspondence between the first derivative of the weight loss and the total ionization current. Approximately four maxima are present in these curves, the major ones occurring at 72, 139 and 350°C.

3. The first products are evolved around 72°C; after this process is complete, approximately 5% of the original sample weight is lost. The major product is maleic anhydride, with lesser amounts of butyraldehyde and water.

4. A second group of products are evolved in the vicinity of 139°C. The weight loss during this evolution amounts to ~ 9% of the original sample. Water is the predominant product; however, carbon dioxide and maleic anhydride are produced at about one-tenth the abundance of water.

5. The above gases appear to be pre-degradation products with actual thermal degradation commencing at 200°C. It is extremely difficult to sort all of the species evolved. Within the major thermal degradation temperature profile, there are perhaps five or more distinct temperature profiles corresponding to the release of one or more products. Mass spectra of furfural and furan can be identified along with the expected carbon monoxide



6. At slightly higher temperatures there is considerable water evolved along with a large ion at m/e 44, probably corresponding to $C_2H_4O^+$ There is not sufficient time resolution of the products to make a positive identification of these products.

7. At still higher temperatures (~ 500°C) there are other products evolved whose spectrum includes m/e 91 and 77 characteristic of aromatic structure.

8. A complete list of solvents, reactants, and proposed polymer structure may aid in the identification of some of the degradation products.

Report III Z - 76

4PAS-A

(Structure not available)

1. Sample Weight 8.23 mg
   Weight Lost (30-680°C) 5.57 mg (i.e., 68%)

2. The first derivative of the weight loss displays three maxima. The first corresponds to the evolution of trapped solvents, namely, N-methyl pyrrolidone (NMP) and water. The former is the major volatile product released. The combined weight loss of these two products is 1.4 mg. NMP onset 45°C; maximum 115°C; complete 220°C.

3. Sulphur dioxide (SO_2) production maximizes at 770° and 500°C corresponding to the latter two maxima in the derivative of the weight loss curve.

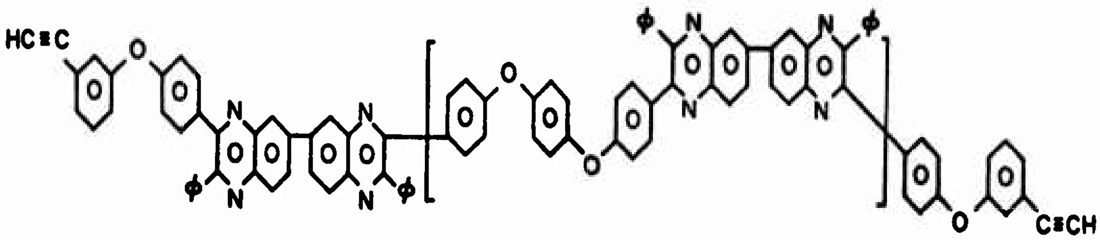
4. Phenol is released at 500°C followed by biphenyl at 515°C.

5. At higher temperatures (~ 570°C) benzene and possibly cresol are evolved.

6. The thermal degradation products SO_2, ϕOH, $C_{12}H_{11}$ and ϕH comprise 75% of the weight loss. The predegradation products, N-methyl pyrrolidone and water make up 25% of the weight loss.

Report III AA - 76

BATQ-H



1. Sample Weight 5.21 mg
   Weight Loss (980°C) 1.86 mg 36%
   Weight Loss (280°C) .05 mg 0.1%

2. Noticeable weight loss commences at ~ 400°C and the rate maximizes at 550°C. The total ionization current, a more sensitive detector, shows an onset at ~ 265°C achieving a maximum at 550°C. There is a shoulder at ~ 690°C.

3. Traces of hydrogen chloride (HCl) are evolved over the temperature interval 250-400°C. This is of importance since it is in the vicinity of the polymerization exotherm; however, there are no Cl atoms listed in the molecular formula so that the origin of HCl is uncertain.

4. The maximum in the total ionization curve at 550°C arises from the evolution of a series of aromatic products that include benzene, toluene and phenol in approximately equal abundance, and benzonitrile and p-cresol (or possibly phenetole) in about one-tenth the abundance.

5. Water is released in high abundance maximizing at 555°C, followed by carbon monoxide at 575°C.

6. Ammonia is produced with a rate maximizing at 700°C.

7. At still higher temperatures (780-850°C) hydrogen evolves. There is evidence for traces of other products as evidenced by m/e 149 ($C_{10}H_{13}O^+$).

8. There are three temperature maxima for a series of ions including m/e 85, 71, 69, 57, 56, 43 and 29. The ion ratios are consistent with long saturated hydrocarbons such as cerane, for example, $CH_3(CH_2)_nCH_3$ where n = 24.

Report III BB - 76

4PAS-C

(Structure not available)

1. Sample Weight 5.89 mg
   Weight Lost (30-1000°C) 3.10 mg

2. N-methyl pyrrolidone evolves at 60°C (max. at 100°C) corresponding to ~ 2.6% of sample weight. Solvent is reduced by factor of ~ 6 compared with 4PAS-A.

3. No water is evolved in predegradation region.

4. Weight loss due to thermal degradation (excluding solvent loss) is 51% for both samples.

5. Degradation products have been listed (Report III Z).

Report IV A - 77

FM-73

(Structure not available)

1. Sample Weight 163 mg
   Weight Loss (30-145°C) 4.1 mg ~ 2.5%

2. Total ionization and derivative of weight loss indicate two regions of product evolution. These occur in the vicinity of 72 and 127°C. Near 72°C the total ionization current displays sharp discontinuities possibly arising from rapid bursts of gas from the sample. The mass spectra at several temperatures in this region indicate constant composition of the evolved gases.

3. At 72°C methyl ethyl ketone and vinyl chloride can be detected. From total ionization currents one can estimate that methyl ethyl ketone production is five times that of vinyl chloride. After the evolution of these gases about 0.65 mg (0.5% of sample) is lost.

4. At 127°C predominantly dimethyl amine is detected along with traces of water. There are other higher molecular weight products evolved with abundance about 1/10 that of dimethyl amine. No positive identification of these components has been made.

SECTION IV

CONCLUSIONS

The technique of thermogravimetric-mass spectrometric (TG-MS) analysis has been applied to the investigation of a series of polymers of interest to the Air Force. Analyses have been conducted during the period April 1976 - March 1977 under Contract F33615-76-C-5152. The data given in this report in conjunction with the individual analyses constitute completion of research on this contract.

APPENDIX

ANALYSIS OF FLUORO-SUBSTITUTED BENZOXAZOLE POLYMERS USING TG-MS TECHNIQUES

ANALYSIS OF FLUORO-SUBSTITUTED BENZOXAZOLE POLYMERS USING TG-MS TECHNIQUES*

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SYNOPSIS

Thermal degradation of a series of 2,5 perfluoroalkyl- and perfluoroalkyl ether-substituted bibenzoxazole polymers has been studied in vacuum using the combined techniques of thermogravimetry and mass spectrometry. Identification and analysis of the evolved gases and their temperature profiles produced during a linear-programmed heating from 30-1000°C have provided correlations between polymer stability and the nature of the fluoro-substitution. The mechanism for primary thermal decomposition in these systems is discussed with particular emphasis on the thermal evolution of carbonyl difluoride.

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I. INTRODUCTION

Mass spectral techniques have been applied for several years in the study of materials.[1-6] Flowers and coworkers[1,2] have used high resolution mass spectrometry to determine the molecular structure by analysis of the thermally stable species evolved during heating. Friedman and coworkers[3,4] have employed a time-of-flight mass spectrometer to analyze the volatile products evolved from polymeric materials during a linearly programmed heating to 1000°C. More recently similar methods have been reported by Risbey and Yergey[5] using a quadrupole mass spectrometer to identify bacteria.

In the present study the volatile products from a series of twelve fluoro-substituted polymers[6,7] have been analyzed using the combined techniques of vacuum thermogravimetry (TG) and quadrupole mass spectrometry (MS) followed by computer treatment of the data. Thermogravimetry provides the quantitative data on the general thermal decomposition and mass spectrometry provides specific, however qualitative, information on the nature of the degradation products. The two sets of data are complementary, thus providing considerable insight into the nature of thermal degradation processes.

Since polymer stability, particularly at elevated temperatures, is an important property for use consideration, TG-MS analysis as outlined in this study can provide general stability criteria which may serve in the design and production of polymers for use over an extended operational temperature range.

II. EXPERIMENTAL

The TG-MS equipment employed in the present study is shown schematically in Fig. 1. The operating conditions are summarized in Table I. Briefly, the vacuum system consists of a pair of 2-in. pumping stations which evacuate the quadrupole mass spectrometer, microbalance, and quartz hangdown tube. With the exception of the balance, the entire system is bakeable to 150°C with ultimate pressure $\sim 5 \times 10^{-7}$ Torr. The sample is suspended in a quartz crucible on a hangdown wire from the microbalance. Temperature is monitored with a Pt/Pt-10% Rh thermocouple located at the sample. There is no line of sight between the sample and ion source of the mass spectrometer, ensuring the detection of predominantly more volatile products. For example, there is considerable discrimination against products of low volatility that condense readily on the cooler walls above the hot zone. The sample is heated by a Marshall furnace at linear rates from 2-8°C/min.; during the present study, samples were heated at 4.2°C/min. Mass spectral scans (m/e 1-300) are completed at a rate of one scan every ten degrees rise in temperature.

Care was taken to prevent the system pressure from rising above 5×10^{-5} Torr to minimize reaction with the sample, to protect the quadrupole, and to minimize the effects of ion scattering within the mass spectrometer. The mass-analyzed ions are detected with an electron multiplier and the signal from the multiplier is amplified and stored on magnetic tape along with the temperature and weight data. Data on the magnetic tape are subsequently analyzed and sorted by a CDC 6600 computer. The data are presented as profiles of weight loss, first derivative of the weight loss, total ionization intensity, and

individual ion intensities as a function of temperature over the range 30-1000°C. In Fig. 2 the weight loss and first derivative of the weight loss for one substituted benzoxazole polymer (Sample 8) are shown. Typical of all the polymers in this series, thermal decomposition and volatile product evolution occur over a relatively narrow temperature interval. The resultant mass spectra represent complex mixtures. Although the mass spectrometer is quite sensitive in detecting products, it is not particularly suited for analysis of mixtures. Consequently, a complete identification of each product is not possible in such complex systems; however, in the present case a good assessment of the major volatile products is possible because of the nature of the products and because of small but distinct differences in the ion intensity-temperature profiles.

III. RESULTS AND DISCUSSION

A. Samples

A series of twelve polymers, synthesized because of their elastomeric properties, have been studied using TG-MS. These are all 2,5 perfluoroalkyl- and perfluoroalkyl ether-substituted bibenzoxazoles. We identify the two locations of substitution as I and II corresponding to chains joining the six-membered benzene rings and five-membered oxazole rings, respectively. The general structure, nature of the substitution, and polymer identification are shown in Table II. The degree of polymerization in these samples varies but is typically in the range 20-50.[9]

The perfluorocarbon substitution consists of a series of either three or eight perfluoromethylene (CF_2) units. Because of the strength of the C-F bond, the polymer samples 1-3 are quite stable; however, the increased

flexibility of perfluoroalkyl ether chains can provide enhanced elastomeric properties. There is a wide range of perfluoroalkyl ether substitution represented in these samples. The simplest, of the form $-CF_2O(CF_2)_2OCF_2-$ can be categorized (1,2,1) according to the number of CF_2 groups linked between oxygen atoms. Similarly, $-(CF_2)_4O(CF_2)_4O(CF_2)_4-$ is categorized as (4,4,4). Using this classification system we have substitution of the form (1,2,1), (1,2,4), (2,5,2), (4,4,4) as well as other types containing trifluoromethyl (CF_3) branches and long perflu roalkyl ether chains. Although a complete set of samples with every combination of perfluorocarbon and perfluoroalkyl ether substitution at the locations I and I is not available, the present set (Table II) contains a wide range of varied substitution.

B. General Results

1. Degradation Temperatures

Using a heating rate of 4.2°/min., the maximum in the degradation rate--as evidenced by the maximum in the first derivative of the weight loss or maximum in the total ionization profile--occurs in the interval 450-600°C. Figure 2 representing polymer sample 8 indicates a maximum at 500°C. Once the degradation commences, it proceeds quite rapidly; the full-width-half-maximum (FWHM) in the first derivative of the weight loss is less than 70°C for all samples.

2. Volatile Products

To a first approximation, each polymer upon degrading releases a series of very similar volatile products. The relative yields of each product, of course, vary from sample to sample; however, the following products are common to each sample:

a. Simple Perfluorocarbons. These are characterized by a series of ions F^+, CF^+, CF_2^+, $C_2F_3^+$, $C_2F_4^+$, $C_2F_5^+$, . . . The temperature profiles of these ions are indistinguishable indicating the concurrent release of a series of simple perfluorocarbons such as C_2F_4, C_2F_6, C_3F_6, and C_4F_8. In general, the temperature behavior of m/e 50, i.e., CF_2^+, can be considered as characteristic of these products. When the original polymers have $-(CF_2)_8-$ substitution, there is increased abundance of the higher molecular weight ions. The ion m/e 286, $C_8F_{10}^+$, is the highest mass characteristic of this series detected in the present study.

Using the criterion developed by Huston, Scott, and Studier[10] to assess the extent of cyclic as opposed to noncyclic pyrolysis products based upon the relative intensities of $C_2F_5^+$ (m/e 119) and $C_3F_5^+$ (m/e 131), we find that polymer samples 1, 2, 3, and 11 possessing $-(CF_2)_8-$ substitution have ratios m/e 119/131 in the range 0.2-0.4 indicative of predominantly cyclic perfluorocarbons as degradation products.

b. Mono-H-Substituted Perfluorocarbons. A series of ions such as C_2FH^+, CF_2H^+, $C_2F_4H^+$, and $C_3F_6H^+$ are observed in these samples. The CF_2H^+ (m/e 51) and $C_2F_4H^+$ (m/e 101) ions indicate the production of CF_3H and C_2F_5H. The C_2FH^+ (m/e 44) is a very abundant ion observed in all spectra in the vicinity of the primary degradation. The absence of mass spectral data in the literature for most partially fluorinated hydrocarbons precludes identification of the product. The abundance of C_2FH^+ appears closely related to m/e 63, $C_2F_2H^+$ and m/e 113, $C_3F_4H^+$ suggesting the formation of C_3F_5H.

The temperature profiles for these ions are not distinguishable. Their rate of production maximizes in the vicinity of the primary

decomposition, namely, 530-600°C. There are some small but reproducible differences in the shape and position of the maximum in these profiles compared to those for the simple perfluorocarbons. The profiles for m/e 50, 51 depicted in Fig. 3 for sample 8 illustrate this effect. In most cases, the profiles maximize within 20 degrees of one another.

c. Hydrogen Fluoride. The ion HF^+, m/e 20, is important in the mass spectra of the degradation products. For the cases of $-(CF_2)_n-$ ($n = 3,8$) substitution at either location I or II, the HF^+ ion represents from 10-25% of the total ionization current, Σ. For all other samples, HF^+ amounts to less than 10% of the total ionization. Comparison of ion intensities with respect to the total ionization current can be deceptive because large changes in the substitution affect both HF^+ and Σ. However, the main point is that HF is a major volatile product.

The temperature profile for HF^+ maximizes in the immediate vicinity of the primary thermal degradation and is not distinguishable from the profiles described above. There is some secondary evidence for HF production from the observation of the SiF_3^+ ion from SiF_4 produced in the reaction (1) of HF with the quartz walls.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \qquad (1)$$

The SiF_3^+ ion, identified unambiguously from isotopic ratios, amounts to only a few percent of the HF^+ ion.

d. Carbon Monoxide. The CO^+ ion from carbon monoxide is also one of the major ions in the observed mass spectra of the products. Its observation in sample 1 indicates formation from decomposition of the

oxazole ring. In the cases where the substitution is of the perfluoroalkyl ether type, there is the added complexity of producing CO^+ as a fragment ion from carbonyl difluoride and other related perfluorocarbonyl compounds as well as from carbon dioxide. The magnitude of CO^+ relative to CFO^+ (abundant ion from perfluorocarbonyl compounds) indicates that carbon monoxide is the major source of CO^+ ions.

The temperature profiles of CO^+ basically reflect the same behavior as the other products discussed above.

e. Carbonyl Difluoride. This is a major thermal degradation product in all of the samples, including sample 1 in which there is no perfluoroalkyl ether substitution. Thus, it can be formed from the oxazole ring as well as from the cleavage of perfluoroether chains. Since CF_2O^+ is the molecular ion, its temperature profile directly shows the release of carbonyl difluoride. These profiles are the subject of a later section concerning carbonyl difluoride production. From the increase in the ratio m/e 47/66 above that expected for COF_2, one can estimate the importance of the higher fluoroalkyl analogues of carbonyl compounds. Particularly in polymers 8, 9, and 12 possessing long-chain perfluoroalkyl ether substitution, there is evidence for increased magnitude of CFO^+ and some higher mass ions such as CF_3CO^+ (m/e 97).

f. Trifluoroacetonitrile CF_3CN. Although not a major product, CF_3CN can be identified from the ions CF_2CN^+ (m/e 76) and CF_3CN^+ (m/e 95). Its temperature profile is similar to that for the perfluorocarbons. The presence of CF_3CN confirms the decomposition of the five-membered oxazole ring.

g. Carbon Tetrafluoride. This does not appear to be a primary degradation product. Its temperature profile is extremely broad indicating the complex rearrangement necessary for its formation. The maximum rate of CF_4 formation occurs in the vicinity of 680-710°C with FWHM of ~ 100 degrees. At 700°C the CF_3^+ ion represents 12-25% of the total ionization current.

3. Undetected Products

In light of the above results and our knowledge of the polymer structures, there are several products that are conspicuously absent.

a. Fluorine. Conceivably F_2 is produced in the degradation but reacts before leaving the polymer. The extreme reactivity[11] of fluorine would support this hypothesis. We observe no mass spectral evidence to substantiate the release of F_2. Furthermore, there is some evidence for the release of small amounts of water during the degradation. Fluorine reacts rapidly with water as shown in reaction (2).

$$2F_2 + 2H_2O \rightarrow 4HF + O_2 \tag{2}$$

There is no mass spectral evidence for the presence of O_2 in any of these samples. Our data would indicate that F_2 is not a thermal degradation product.

b. Cyclic C_6 Products. With one exception--namely, the tentative assignment of m/e 186 as $C_6F_6^+$--there is no mass spectral evidence for any cyclic C_6 products characteristic of the six-membered ring. The mass spectral evidence is consistent with the occurrence of primary thermal degradation at the locations I and II of perfluorocarbon substitution and the five-membered oxazole ring.

c. Fluoro-Formaldehyde. The relatively large abundance of products such as HF, CF_3H, C_2F_5H, . . . would suggest the possibility of fluoroformaldehyde; however, we observe no HCOF produced. It appears that the mechanism for carbonyl difluoride production is distinct from the mechanism for simple perfluorocarbon formation. This is contrary to any suggestion that there are random C-C, C-F, C-H, and C-O bond cleavages which yield some statistical distribution of stable products.

4. Char Remaining at 1000°C

For nine of the twelve polymers, we have absolute weight data concerning the amount of char relative to the sample weight. This is summarized in Table III. Based upon the mass spectral evidence that there are no aromatic cyclic C_6 products, one could estimate that the ratio of char to the original sample weight is reflected by the ratio C_{12}/M where C_{12} is the molecular weight of twelve carbon atoms and M the molecular weight of one polymer unit. These have been calculated and summarized in the last column of Table III. Considering the gross approximation made in this calculation, there is a good correlation between the calculated and observed ratios.

C. Examination of Carbonyl Difluoride Production

1. Empirical Analysis

Carbonyl difluoride can be monitored unambiguously because the stable molecular ion is both abundant and uniquely assigned. The temperature profiles of CF_2O^+ for each of the twelve samples are shown in Figs. 4-6. The profile for sample 7 depicts the CFO^+ (m/e 47) ion rather than CF_2O^+ because of low intensity[12] at m/e 66.

In samples 1-4, substitution at location II remains fixed, $-(CF_2)_8-$, while changes are made in location I from a direct bond between the benzene rings to short and long chain perfluoromethylene groups and finally to a (2,5,2) ether. The temperature profiles of COF_2 display no significant differences; in each case, the maximum lies between 550-590°C. Note also that the profiles are relatively narrow (FWHM < 60 degrees) as is observed for almost all of the volatile products released in the region of thermal degradation. To a first approximation, the nature of the substitution at location I plays a relatively minor role in determining the course of degradation. In addition, within the temperature interval 550-580°C, all of the major products listed in Section B are released.

Samples 5 and 12 contain a (2,5,2) ether and (4,4,4) ether substitution, respectively, at location II. Again, the maximum in the rate of COF_2 production falls within the interval observed above.

The profiles for samples 6-9 display two distinct maxima. In each case, the second maximum corresponds quite closely in position and shape to the profiles outlined above. The first maximum lies in the temperature range 510-540°C. In each case, there is 50-60 degrees difference between the maxima permitting partial resolution of each profile. The separation is of the same order of magnitude as the FWHM of either profile. The fact that these peaks can be resolved indicates that the process responsible for the first peak proceeds past its maximum rate before the second process dominates.

Empirically there is one common feature present in samples 6-9 that is not present in samples 1-4 and 5,12. In each case, there is perfluoroalkyl ether substitution at location II in which there is an oxygen atom β to the five-membered oxazole ring. The samples 10 and 11 have ether substitution

of the form (1,2,1) at location II; each then has an oxygen β to the oxazole ring and displays a maximum within the lower temperature interval 510-540°C. If a second maximum exists (there is some indication of a second peak in sample 11 shown in Fig. 6), it is either unresolved or relatively unimportant.

We can summarize COF_2 formation in the following empirical rules that satisfy the set of twelve polymers studied:

a. COF_2 can be formed utilizing the oxygen from the oxazole ring.

b. The temperature for COF_2 production is relatively unaffected by large changes in the substitution at location I linking the six-membered benzene rings.

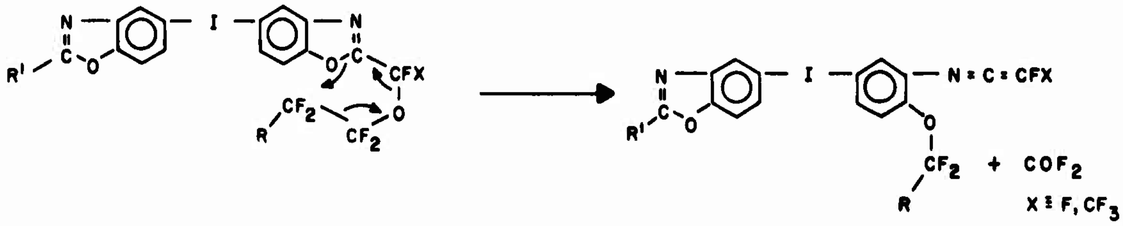
c. Substitution at location II linking the five-membered oxazole rings of the form $-(CF_2)_n-R-$ where n = 2, 3, 4, or 8 behave indistinguishably with the rate of COF_2 maximizing within the temperature interval 550-580°C.

d. Substitution at location II of the form $-CF_2-O-R-$ or $-CF(CF_3)-O-R$ in which there is an oxygen β to the oxazole ring has a significant effect on the thermal stability manifested in a lower activation energy process occurring with a maximum rate in the temperature interval 510-540°C.

2. Proposed Mechanism

The fact that COF_2 is produced in the fluoro-substituted bibenzoxazoles in the range 550-580°C, precisely the temperature region where other products such as CO, C_2F_4, CF_3CN, . . . are observed, suggests that the oxazole ring opens and that there is local cleavage of many bonds resulting in rapid breakdown of the oxazole ring and the attached fluoro-substituents.

Presumably at ~ 50° lower temperature where there is insufficient energy for rapid bond cleavage, there is the possibility of an alternate lower-activation-energy route when there is fluoroether substitution having an oxygen β to the oxazole ring. We propose the following rearrangement involving a symmetric six-membered ring intermediate



(3)

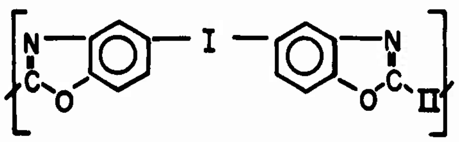
Once the oxazole ring has opened and COF_2 is released during the six-centered reaction, there are many other reactions possible. Clearly subsequent formation of perfluoroacetonitrile CF_3CN and more COF_2 may be expected. The advantage of having an oxygen β to the ring permits a symmetric cyclic intermediate. When oxygen is γ to the ring, although a similar but nonsymmetric ring rearrangement as in (3) could be envisaged for COF_2 formation, the results would indicate that the process is too slow to be detectable. Similarly we have looked carefully for evidence for C_2F_4 production via an analogous rearrangement in the case of long perfluoromethylene substitution on the oxazole ring, but have not observed a significant effect.

The resolution of two peaks with FWHM ~ 60 degrees of about the same intensity requires a separation in excess of 30 degrees. Thus, the present techniques as applied to this system are only capable of detecting effects of the order of magnitude observed above. They certainly would not detect such effects if the maxima differed by only 20 degrees.

3. Discussion of Samples 10 and 11

As can be seen in the temperature profiles in Fig. 5, samples 10 and 11 do not display a resolved maximum in the region 550-580°C as observed in the other ten samples. These two samples share the common substitution of (1,2,1) ether substitution at the oxazole ring. Subsequent to the rearrangement (3) there is the possibility of a second elimination of COF_2 from the other end of the chain.[13] The elimination of two molecules of COF_2 would open both oxazole rings and eliminate most of the perfluoroalkyl ether substitution with the result that the probability of further elimination of COF_2 at higher temperatures may be greatly reduced.

D. Thermal Degradation Mechanism



We propose the following mechanism to account for the observed results at a heating rate of 4.2°/min.

1. As the temperature is raised above 400°C, the lowest-activation-energy process, (3), occurs to evolve COF_2 when the substitution at II has an oxygen atom β to the oxazole ring. The process continues with a rate maximizing within the temperature interval 510-540°C. Eventually, as the number of new reaction centers diminishes, the rate for COF_2 formation drops.

2. At temperatures around 500°C, bonds within the substituted perfluoro and/or perfluoroalkyl ether linkages at I or II and bonds within the five-membered oxazole rings can acquire sufficient energy to result

in C-C, C-F, and C-O bond cleavages to produce a series of free radicals such as $F^{\cdot}$, $CF_3^{\cdot}$, and $C_2F_5^{\cdot}$. These can promptly abstract hydrogen atoms from the six-membered rings to form HF, CF_3H, and C_2F_5H. In addition, other stable products such as C_2F_4, C_3F_6, C_4F_8, etc., are produced as a result of cleavage within the perfluoromethylene chains. Also trifluoroacetonitrile, carbon monoxide and carbonyl difluoride are formed. The maximum in the rate of these processes is fairly well defined within the temperature interval 550-580°C. Rapidly most of the fluoro-substituted chains and oxazole rings are destroyed leading to a sudden completion of the primary phase of thermal degradation around 620°C. Generally completion of this phase occurs over slightly more than a 100 degree interval with almost one-half of the degradation occurring within a 60 degree interval.

3. By the time the sample temperature reaches 600°C, almost the entire degradation process is complete. A slow rearrangement occurs to produce carbon tetrafluoride. The rate maximizes at ~ 700°C then drops slowly.

4. The thermogravimetric results and the mass spectrometric analysis of the degradation products indicate that the char consists primarily of carbon atoms that originated as the six-membered rings in the original bibenzoxazole sample.

IV. CONCLUSIONS

By applying the combined techniques of TG and MS to study the thermal degradation of a series of perfluoroalkyl- and perfluoroalkyl ether-substituted bibenzoxazoles, an overall mechanism has been proposed. In addition, some correlations governing the relationship between polymer

structure and stability have been noted. Basically the stability is strongly dependent upon the nature of the perfluoroalkyl ether substitution at the position β to the oxazole ring. The sensitivity of mass spectral detection of trace amounts of carbonyl difluoride produced at relatively low temperatures is considerably greater than that for the thermogravimetric detection of weight loss in this region. In addition, the weight loss is non-specific, whereas the mass spectrometric detection of this product and its direct correlation to thermal degradation is specific.

In conclusion, TG-MS can be a very sensitive means of probing thermal stability.

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12. The low intensity at m/e 66 in this experiment resulted from excessive discrimination against higher mass ions. The most abundant fragment ion CFO^+ from carbonyl difluoride represents the temperature profile for carbonyl difluoride. In most cases, the behavior of CFO^+ is indistinguishable from CF_2O^+. In general, CF_2O^+ is preferred because there is some lack of definition in the shape of CFO^+ as a result of contributions from heavier perfluorocarbonyl products.

13. A second rearrangement in this case would involve a non-symmetric six-membered ring intermediate.

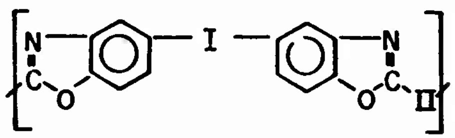
Table I

Instrumental Conditions

Pumping Speed (at ion source)	40 ℓ s^{-1}
Pressure (no heat)	1 x 10^{-6} Torr
Pressure (maximum)	5 x 10^{-5} Torr
Sample Weight	3-5 10^{-3} g
Hangdown Tube	quartz
Balance Sensitivity (Cahn RH)	± 10 10^{-6} g
Sample Temperature (Pt/Pt-10% Rh)	30-1000°C
Heating Rate	4.2°/min
Quadrupole (Granville Phillips Spectroscan 400)	m/e (1-300)
Ionizing Voltage	70 eV
Computer	CDC 6600

Table II

Fluoro-Substituted Benzoxazole Structures



Location I	Location II	Identification Number
-	$(CF_2)_8$	1
$(CF_2)_3$	$(CF_2)_8$	2
$(CF_2)_8$	$(CF_2)_8$	3
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_8$	4
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_2O(CF_2)_5O(CF_2)_2$	5
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$(CF_2)_4O(CF_2)_2O(CF_2)$	6
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(CF_3)O(CF_2)_5OCF(CF_3)$ 75% $(CF_2)_4OCF(CF_3)CF_2OCF(CF_3)$ 25%	7
$(CF_2)_2O(CF_2)_5O(CF_2)_2$	$CF(CF_3)(OCF_2CF(CF_3))_mO(CF_2)_5O(CF(CF_3)CF_2O)_nCF(CF_3)$ $m + n = 5$	8
$(CF_2CF_2O)_3(CF_2)_5O(CF_2)_2$	$CF_2(OCF_2CF_2)_mO(CF_2)_5O(CF_2CF_2O)_nCF_2$ $m + n = 7$	9

Table II (continued)

Location I	Location II	Identification Number
$(CF_2)_3$	$CF_2O(CF_2)_2OCF_2$	10
$(CF_2)_8$	$CF_2O(CF_2)_2OCF_2$	11
$(CF_2)_2OCF_2\underset{\displaystyle CF_3}{\underset{\vert}{CF}}O(CF_2)_2O\underset{\displaystyle CF_3}{\underset{\vert}{CF}}CF_2O(CF_2)_2$	$(CF_2)_4O(CF_2)_4O(CF_2)_4$	12

Table III

Char Remaining After Pyrolysis to 1000°C

Sample	Char Weight/Sample Weight	C_{12}/M
1	0.17	0.23
2	0.21	0.18
3	0.15	0.14
5	0.10[1]	0.12
6	0.09	0.13
8	0.05	0.07
10	0.20	0.23
11	0.21	0.17
12	0.07	0.09

[1] average of six separate runs

FIGURE CAPTIONS

Figure 1. Schematic of instrument

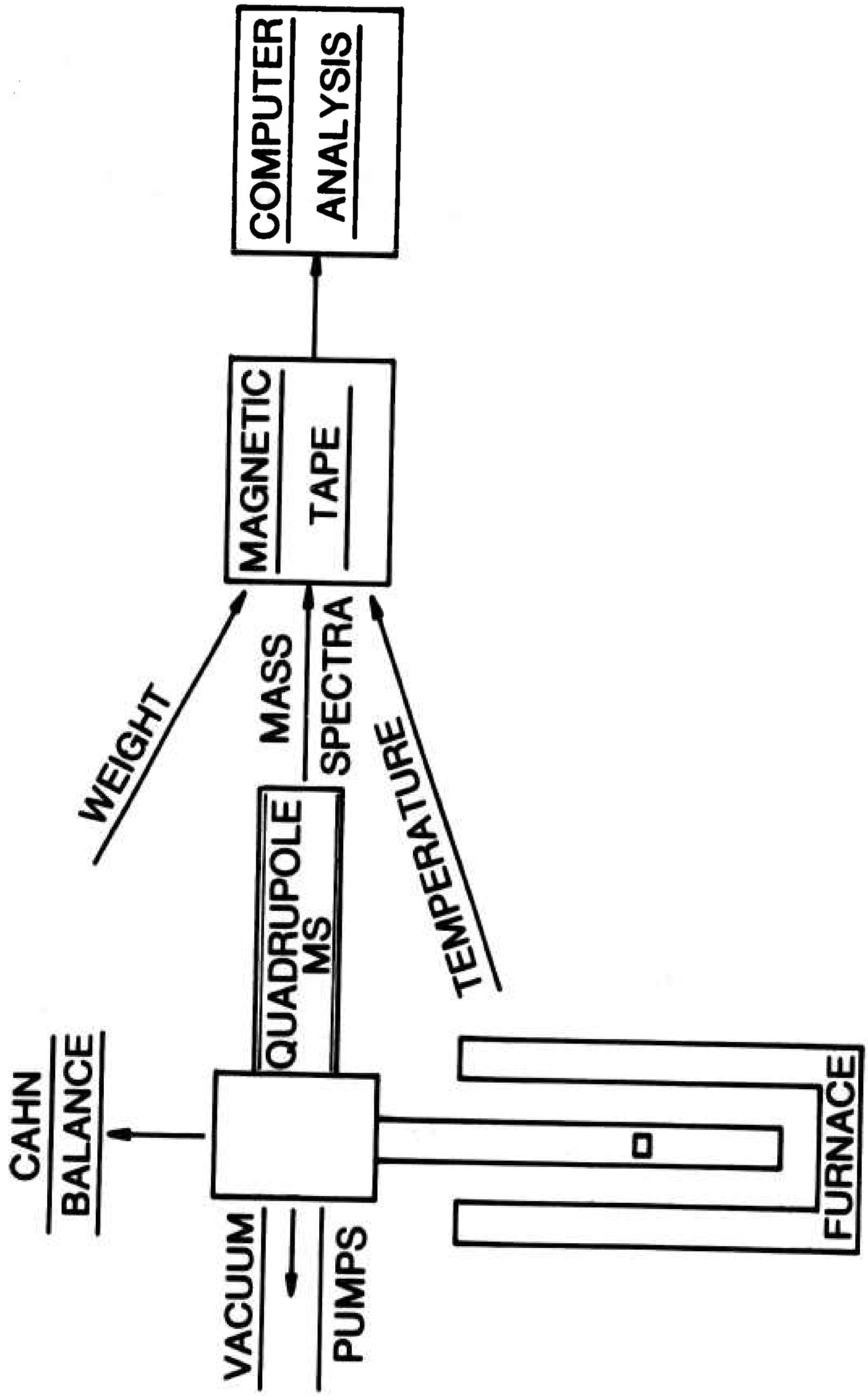
Figure 2. Weight loss and first derivative of weight loss for sample 8 as a function of temperature

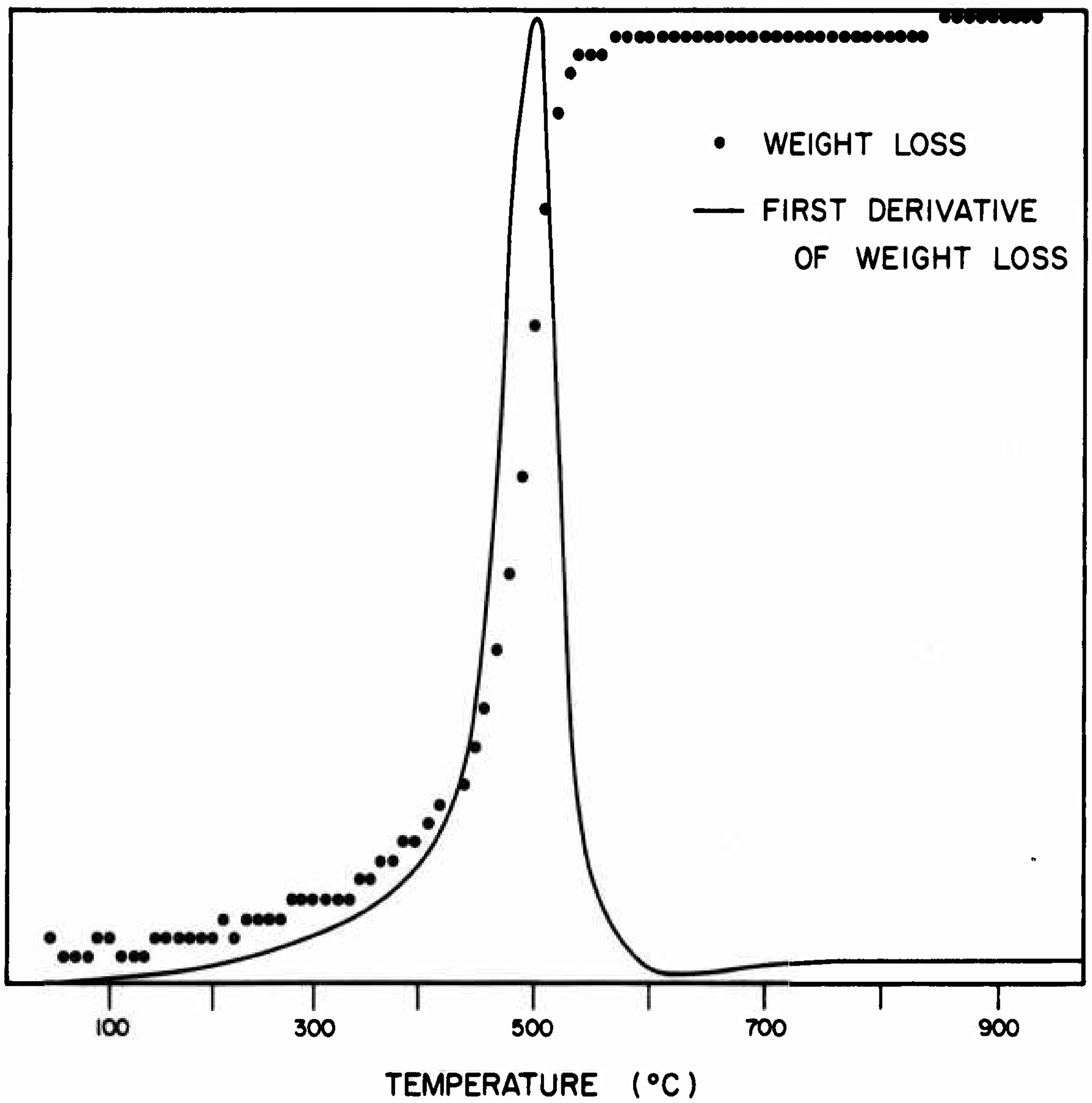
Figure 3. Temperature profiles for m/e 50,51 in sample 8

Figure 4. Temperature profiles of carbonyl difluoride production in samples 1-5

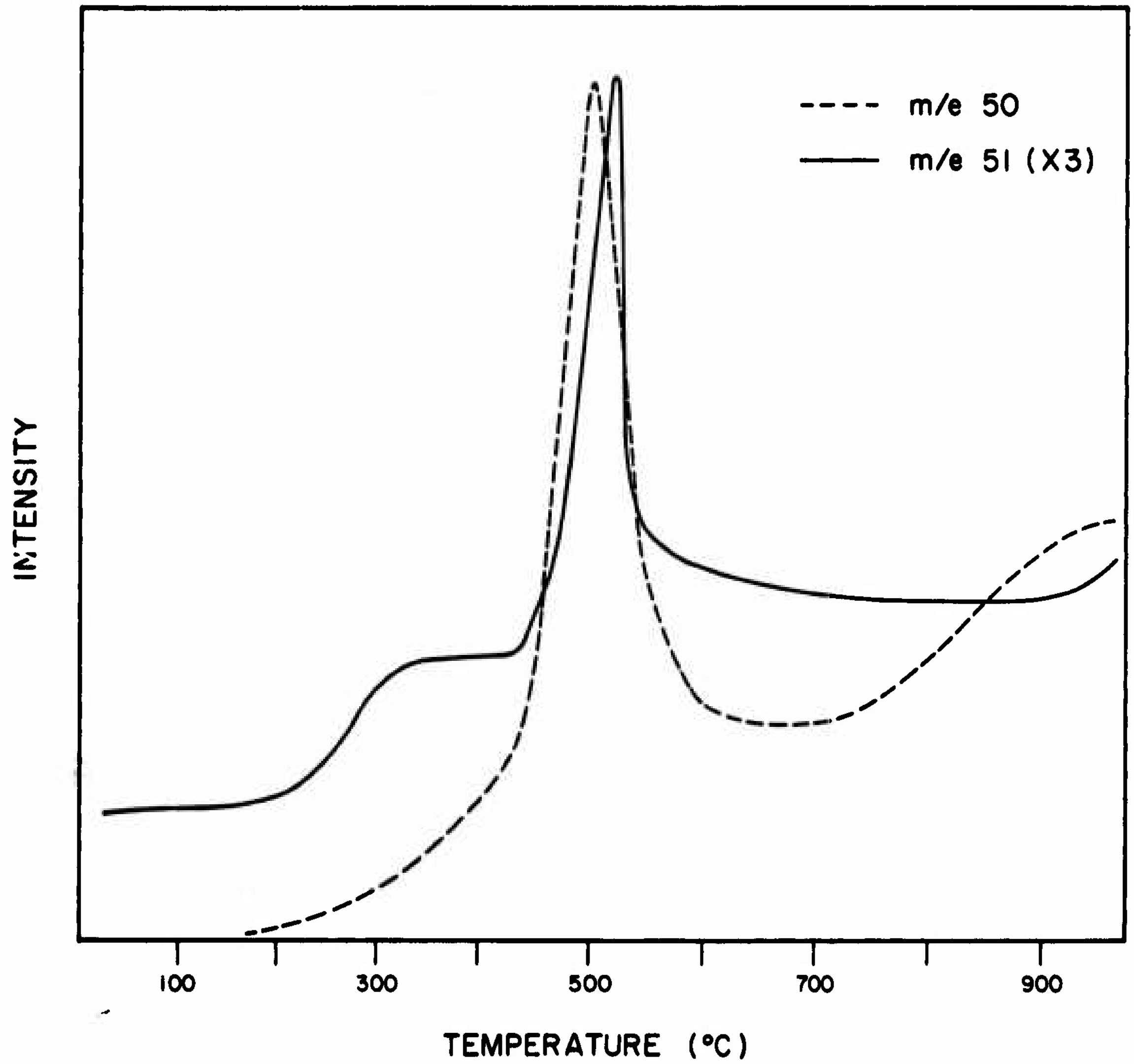
Figure 5. Temperature profiles of carbonyl difluoride production in samples 6-8

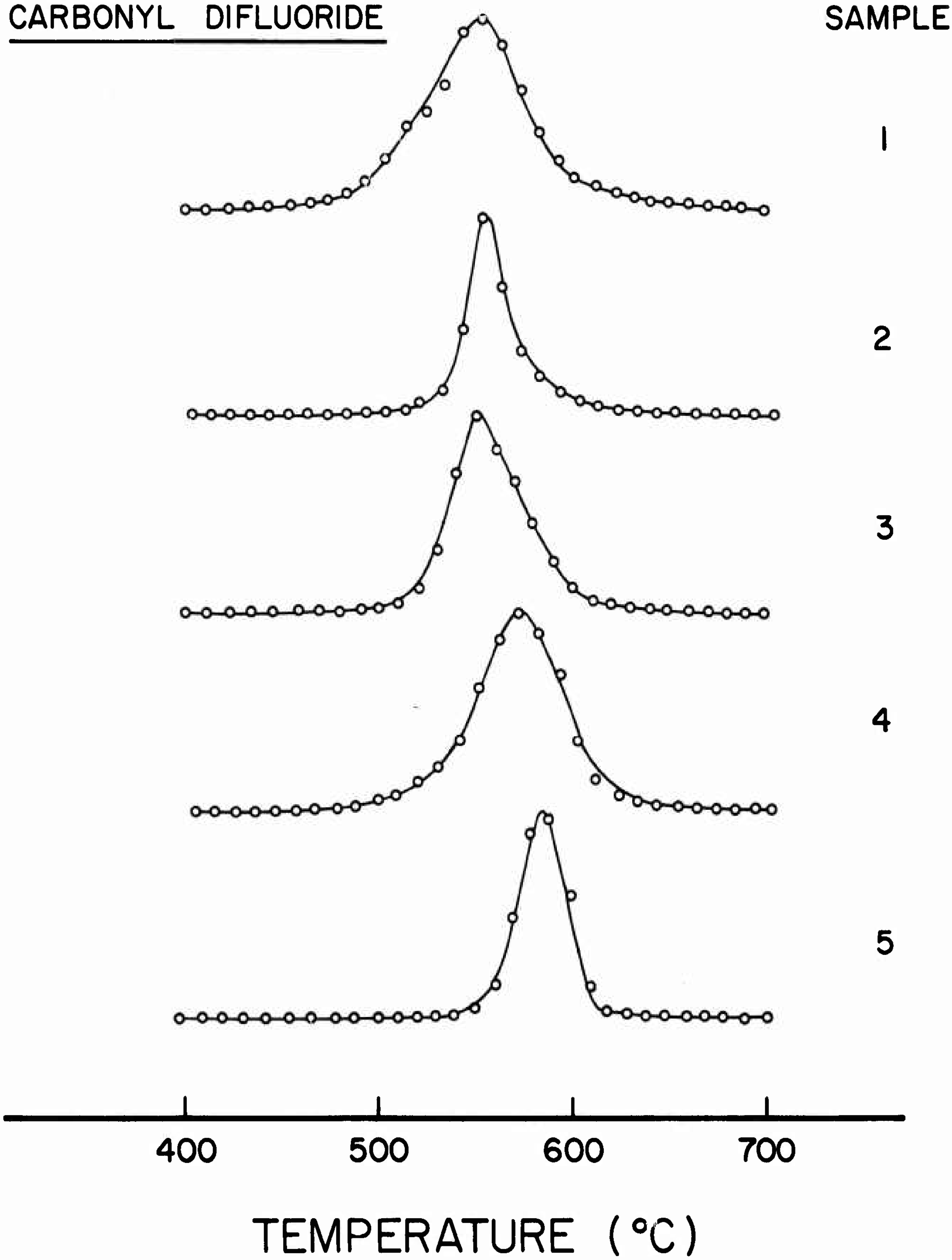
Figure 6. Temperature profiles of carbonyl difluoride production in samples 9-12

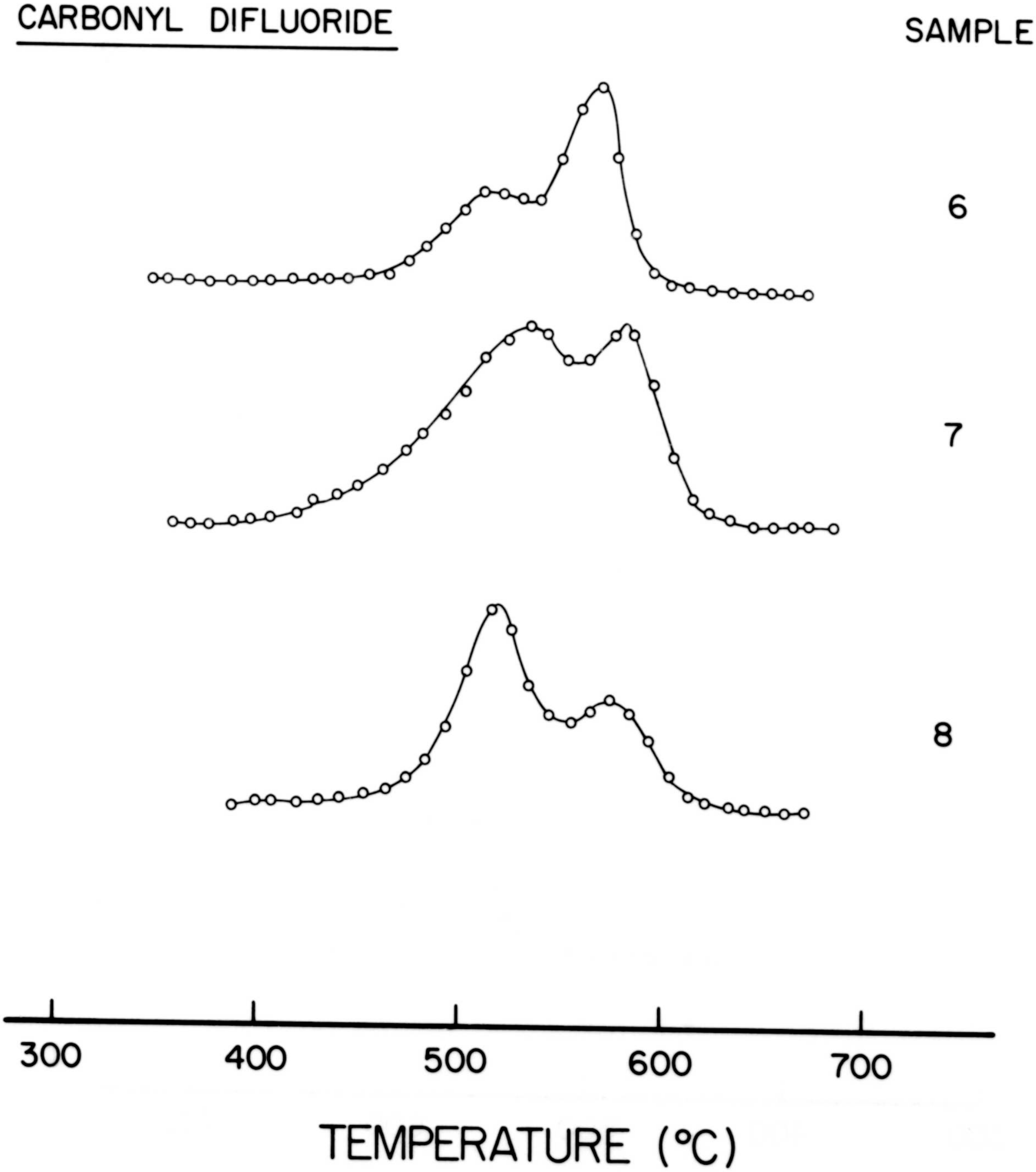

COMPUTER ANALYSIS
MAGNETIC TAPE
WEIGHT
MASS SPECTRA
TEMPERATURE
QUADRUPOLE MS
CAHN BALANCE
VACUUM PUMPS
FURNACE

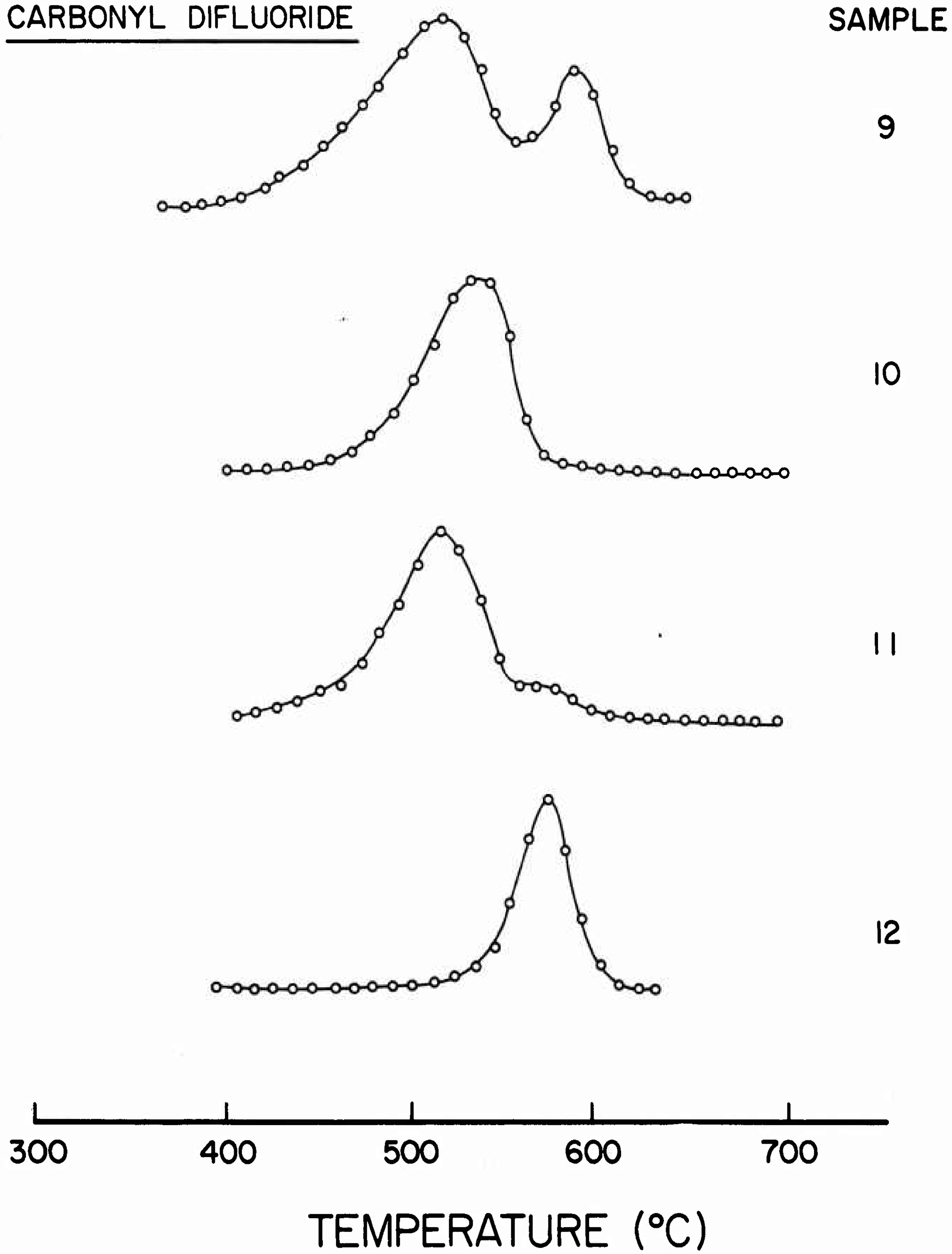


WEIGHT LOSS
FIRST DERIVATIVE OF WEIGHT LOSS
100
300
500
700
900
TEMPERATURE (°C)


m/e 50
m/e 51 (X3)
INTENSITY
100
300
500
700
900
TEMPERATURE (°C)


CARBONYL DIFLUORIDE
SAMPLE
1
2
3
4
5
400
500
600
700
TEMPERATURE (°C)


CARBONYL DIFLUORIDE
SAMPLE
6
7
8
300
400
500
600
700
TEMPERATURE (°C)



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